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Reactive Transport of Silanes in Cement Based Materials

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Abstract

Silanes are often used for impregnating cement based materials to render their surface water repellent. The agents are sprayed on the concrete surface and transported into the porous material by capillarity. During the transport different chemical reactions take place (hydrolysis, condensation, sorption). Neither the kinetics nor the mechanism of these reactions as well as the influence of transport processes on them are fully understood. Different batch experiments have been performed in order to characterise the kinetics of the hydrolysis. In this way the hydrolysis reaction-constants have been determined for varying types of silanes and cement based materials. The results obtained showed that the surface-tension of the water-silane-mixture varies as reaction proceeds, an effect which had not been previously reported. Sorption experiments revealed an important influence of the type of silane on the amount of absorbed silicon compound and its bonding strength to the surface. In addition reactor-experiments have been performed to examine the reactive transport of silanes in cement based materials in a model-system under controlled conditions. These experiments are useful for understanding the interaction that occurs between silane and cement based materials when these are hydrophobised.

Keywords: silanes, reactive transport, hydrolysis, kinetics, reactor experiments, batch experiments, surface tension, sorption

1 Introduction

Cement based materials are frequently affected by physico-chemical interface processes resulting from their ability to take up liquids by capillarity. Mainly water and chemicals dissolved in water (e.g. chlorides and sulfates) are transported through the pores into the matrix of the cement based materials. To avoid degradation phenomena by the uptake of aqueous solutions, cement based materials are frequently impregnated with silicon-organic compounds (silanes). These are transported into the porous material rendering it hydrophobic [1]. In practice, silanes are sprayed on the concrete surface from where they are transported into the porous material by capillarity. During transport different chemical reactions take place which lead to the formation of a water repellent silicone resin (polysiloxane) on the inner surface of the capillary structure.

However, the complex chemical reactions of the silanes and the interactions with the surface of the treated materials are not fully elucidated [2, 3]. According to the current understanding the chemical reactions of alkoxy silanes in solid substrates take place as presented in Figure 1. Under normal climatic conditions water is adsorbed on the inner pore surface of the cement based material. In the presence of water alkaline hydrolysis leads to a split of the Si-OR$_1$ bonding resulting in the formation of a silanol accompanied by the release of an alcohol (Figure 1a). Further condensation of the Si-OH groups generates siloxane bonds (Si-O-Si) forming a three-dimensional silicone resin with strong water repellent properties (Figure 1b). Only in theory the hydrolysis and condensation reactions occur consecutively. In reality the reaction steps take place simultaneously so that different intermediates are generated: silanols, silane diols and silane triols, besides partly condensed monomers [2]. When the siloxane molecule is fixed to the surface of the cement based material, the alkyl group R$_2$ is oriented towards the open pore space and creates a hydrophobic film on the mineral surfaces (Figure 1c). However, not only a chemical adsorption as described above is possible, but also a physical adsorption of siloxanes to mineral particle surfaces may occur [4, 5]. The real situation in practice is even more complex, because transport processes take place at the same time as the chemical reactions do, which influence each other (reactive transport processes). Therefore, the silane reaction described above is greatly simplified, as the influences of the type of silane, the cement based material, transport processes or changing pH-values (carbonatation) are not taken into consideration [6].

The analyses of the processes taking place during the reactive transport of silanes are not only important for academic but also for technical reasons. The latter parameters determine significantly the penetration depth of the water repellent agent and hence the performance and long-term behaviour of hydrophobic treatments.

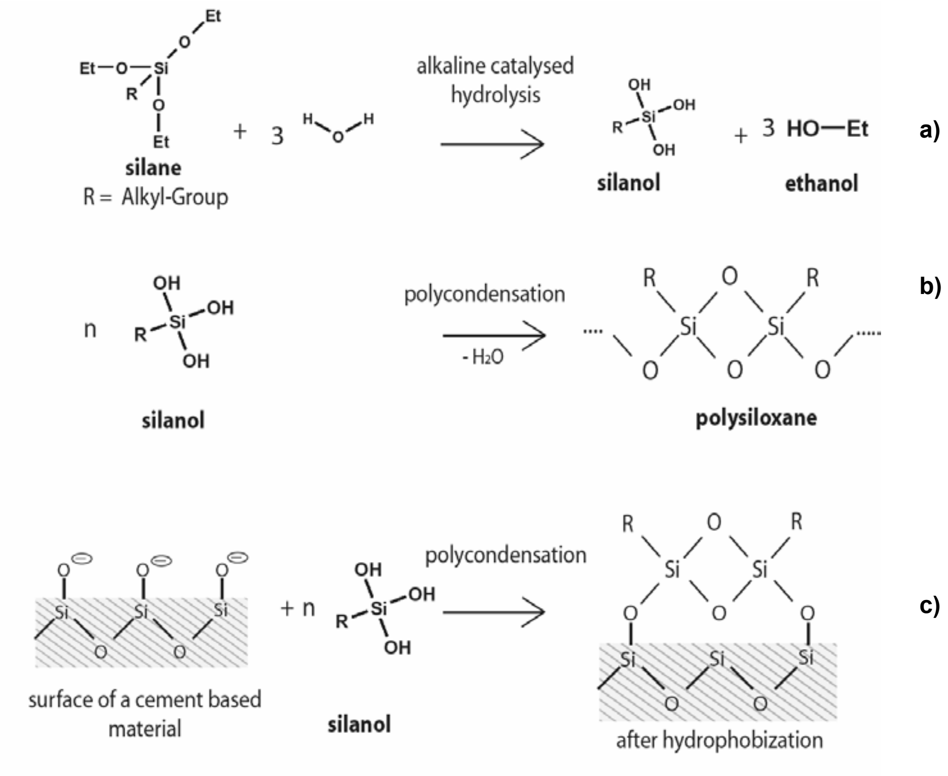

Figure 1: Model for the mechanism of alkaline catalysed reaction from silanes to polysiloxanes in cement based materials (reaction a: three ethanol molecules are released and silanol is formed; reaction b: polycondensation leads to a polysiloxane, which can be bonded (reaction c) to the surface of a cement based material

The objective of this study is to characterise the chemical interactions between silicon organic compounds and cementitious materials. With these results a molecular level model could be developed in order to predict the behaviour of these water repellents and to optimize the performance of new synthesized silanes.

2 Methodology

Different experimental set ups were developed for examination and characterisation of the reaction mechanism of silanes applied on cement based materials. Both batch and reactor experiments were carried out. The influence of different factors such as the length of the alkyl group, silane concentration, structure of the cement based material and pH-value were studied.

Because of the on-going chemical reactions in the **batch-experiments**, the composition of the reaction mixture changes continuously until a stable equilibrium is reached. In each experiment, 100 ml of water based solution (with a defined pH-value) was mixed with a defined amount of silane and, in some cases, with 10 g of ground solid material (e.g. concrete with a w/c-ratio of 0.4, hardened cement paste and quartz). These mixtures were shaken or stirred for some hours or days (according to the structure of the silane). The structure and amount of the reaction products were then analysed.

For this purpose, the velocity of the ethanol release, which corresponds to the kinetics of the **hydrolysis**, was analysed by wet chemical analysis, as described next. After mixing 1 mL of the mixture described above with 1 mL of a 10% $K_2Cr_2O_7$ solution (at pH = 1) an oxidation of the ethanol takes place resulting in a colour change of the solution. The colour change, which is proportional to the released ethanol concentration, was measured with an UV-VIS-spectrophotometer (Lambda 16/Perkin-Elmer; wavelength: 600 nm).

Preliminary experiments had shown that during the hydrolysis and polycondensation the **surface tension** of the water-based liquid phase changes. These changes, that correspond to the formation and decomposition of intermediary products (e.g. silanols), were analysed by means of a Bubble Tensiometer (SITA science Line t60/SITA Messtechnik GmbH, 21 °C) in the online-mode.

The **sorption of silicone compounds** on the matrix (e.g. ground quartz, hardened cement paste, concrete) was examined by Fourier Transformation Infra-Red (FTIR) spectroscopy (Spektrum One/Perkin-Elmer, KBr method, solid transmission). FTIR-spectra in the wavelength range from 2850 cm^{-1} to 2965 cm^{-1} were recorded. For quantitative data evaluations, the area of the peak attributed to the CH_2/CH_3-group was calculated with a software application [4].

The **reactor experiment** was based on a HPLC set up (High Performance Liquid Chromatography) and is suitable for the investigation of reactive transport processes. For this purpose, the HPLC column was filled with ground solid material such as powdered concrete or quartz (stationary phase). The mobile, liquid phase is an aqueous solution saturated with respect to both calcium hydroxide and calcium carbonate. This eluent was pumped through the column at a continuous flow rate (0.05 mL/min). After injection of the test substance (e.g. 1 mL of pure silane) kinetics of the hydrolysis was determined by quantifying the released ethanol collected at the end of the column. This was assessed according to the wet chemical method described above. Upon completion of the experiment the amount of siloxane absorbed by the solid phase compound was determined by FTIR analysis at different depths of the column [6]. The reactor experiments serve as model for real applications and represent a missing link between batch experiments examining the basic chemical reactions and absorption experiments on real concrete blocks which were not performed in this study but are described in the literature [4].

3 Results

3.1 Batch experiments

3.1.1 Hydrolysis

The kinetics of hydrolysis depends strongly on the silane structure as well as the properties of the solid phase and the pH-value of the liquid phase. This paper only discusses the influence of the molecular structure. In Figure 2 the results of the batch experiments for triethoxysilanes with different alkyl groups are presented.

The results show that ethanol release is complete. But the time for a complete decomposition depends on the type of hydrophobic group of the silane. For silanes with a small alkyl group such as propyltriethoxysilane and iso-butyltriethoxysilane, hydrolysis is complete after one hour at most, whereas in the case of steric hindered silanes, such as the two isomers of octylsilane, it takes more than one week.

3.1.2 Surface tension

The solubility of silanes depends on their chemical structure and increases during the hydrolysis due to the formation of ethanol and silanols. According to the hypothesis formulated by Gerdes [4], the capillary transport of silanes in cement based materials is influenced by the migration of the water soluble species into the water film which is adsorbed on the inner pore surface. Due to the enrichment of these species in the water film the interfacial tension between silane and water decreases. This effect influences strongly the transport properties because the interfacial tension is the driving force for capillarity. Therefore, the time-dependent changes in the surface tension have been determined for the studied silanes.

Results obtained from measurements with a tensiometer revealed that the surface tension of a liquid phase (pH 12.8) after the addition of silane varies during reaction in a characteristic way, as shown in Figure 3. At the beginning of the experiment the surface tension is 72 mN/m (characteristic for water). After the addition of silane (0.008 mol/L) the surface tension decreases rapidly and reaches a value that is characteristic for each of the selected silanes. For instance, the measured surface tension for n-propyltriethoxysilane is in the range of 44 mN/m while for iso-octyltriethoxysilane it is around 52 mN/m. After a given time span, the surface tension reaches a constant value in the range of that of water. Both the time span and the actual final surface tension value depend on the silane structure. For n-propyltriethoxysilane the surface tension increases after approximately 20 min while for n-octyltriethoxysilane it takes 4.5 hours to increase after addition of the silane to the solution.

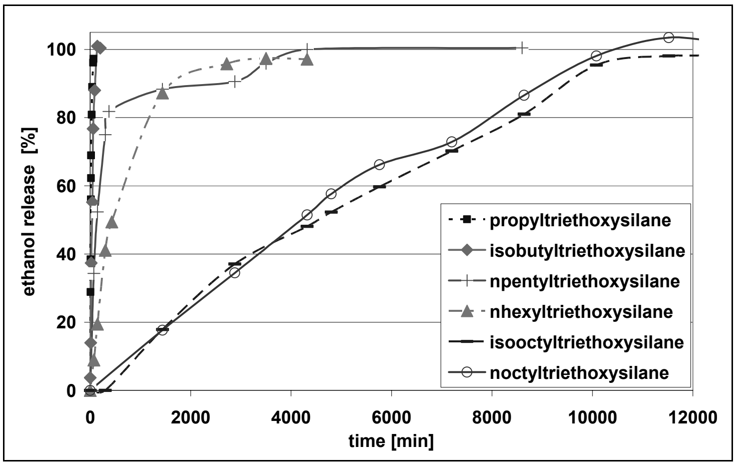

Figure 2: Ethanol release as function of time for mixtures of aqueous solution (pH 12.8) and different triethoxysilanes (0.03 mol/L); the ethanol release is related to the theoretical amount in case of quantitative reaction

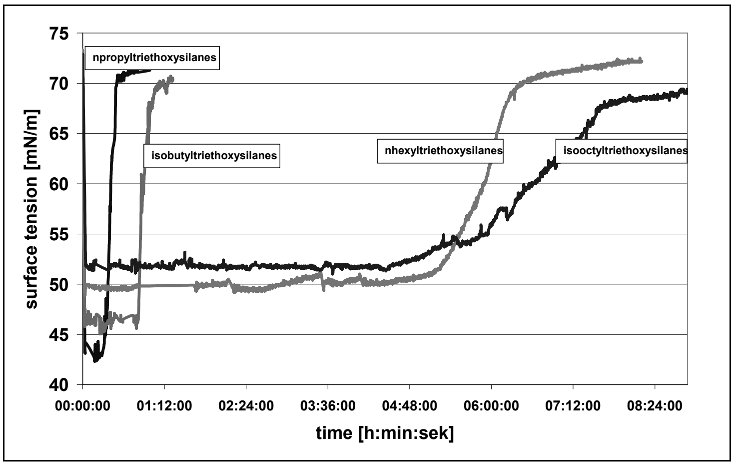

Figure 3: Time-dependence of the surface tension of an aqueous solution (pH 12.8) after the addition of the selected silanes (0.008 mol/L)

3.1.3 Sorption of silicon compounds

Condensation of the Si-OH groups generates siloxane bonds (Si-O-Si) forming a three-dimensional silicone resin in the case of tri-functionalised silanes. Silanol groups also react with terminal OH-groups which are located on the surface of the cement based material [5] leading to the formation of a silicone film bonded to the mineral surface. In order to investigate the properties of the film the amount of polysiloxane chemical linked to the substrate was analysed by FTIR for the selected silanes at different concentrations (0.0003 – 0.1 mol/L). The results are plotted in Figure 4. The adsorption curves of the tested silanes show a similar shape. The higher the concentration of the silane in the solution, the more polysiloxane is adsorbed on the concrete. However, there exists a critical silane concentration (c_1) above which the adsorbed amount of polysiloxane (q_{max}) will not increase. For each silane, a characteristic critical concentration (c_1) value and a maximum amount of adsorbed polysiloxane (q_{max}) can be determined. Furthermore, the results indicate that the q_{max} value increases with the number of C-atoms of the alkyl group.

Extraction with hexane of the solid phase to which the silicon polymer was adsorbed was evaluated by FTIR analysis. The results showed that, in contrast to polysiloxanes having a short alkyl group attached to silicon, those with long alkyl groups could be partly extracted by hexane. However, after three months of conditioning under dry conditions no polysiloxane, neither with short nor with long alkyl groups, could be removed from the solid material by hexane.

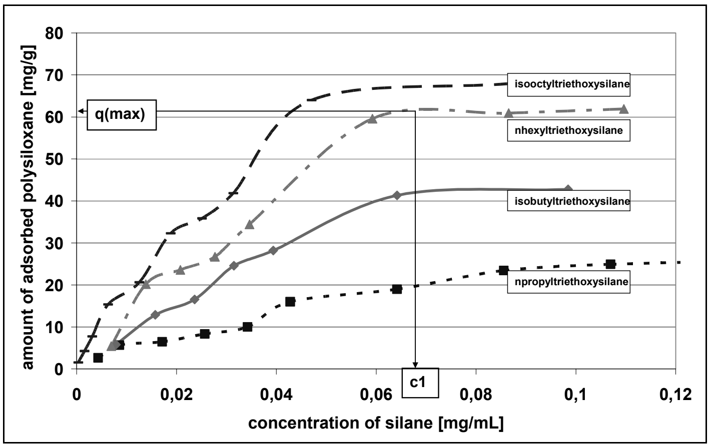

Figure 4: Absorption of polysiloxane to concrete powder for different silane concentrations (pH-value of the liquid phase: 12.8)

3.2 Reactor experiments

In practice, silanes are transported into the concrete by capillarity. As mentioned, the chemical reactions influence the transport process by the formation of water soluble species, while the transport process as such influences the local chemical equilibriums. To investigate the reactive transport properties different reactor experiments were carried out.

The amount of ethanol, released by hydrolysis of ethoxysilanes, is plotted in Figure 5. For comparison the breakthrough curve for pure ethanol is also given.

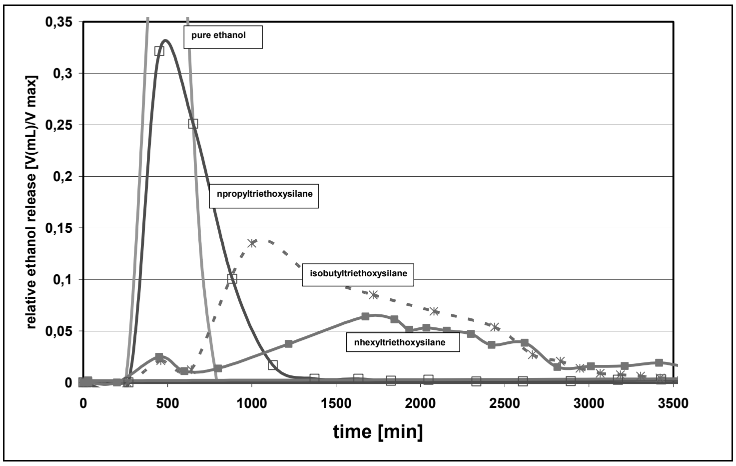

Figure 5: Time-dependence of ethanol release for different ethoxy functionalised silanes. The ethanol release is normalized to the maximum amount in case of quantitative reaction. Pure ethanol breakthrough curve is plotted as reference.

The curve of ethanol released from the hydrolysis of n-propyltriethoxysilane shows a sharp peak, similar to the one of pure ethanol with a maximum at about the same time. The longer the alkyl groups, the lower the maxima of the wider becoming peaks in the ethanol release curve. The total amount of ethanol, as reflected by the peak area, decreases. For iso-butyltriethoxysilane and n-hexyltriethoxysilane two maxima can be observed, a first after approximately 500 min and a second after respectively 1000 and 1700 min. The reason for the appearance of the first peak has as yet to be elucidated.

Figure 6 shows the polysiloxane distribution in the solid phase of the column analysed by FTIR spectroscopy. The longer the alkyl group, the stronger is the polysiloxane adsorbed to the solid phase. Therefore, n-hexyltriethoxysilane is absorbed on the first half of the column, while shorter alkyl groups are absorbed lower down in the column.

The results reveal hence a strong influence of the type of alkyl group on the hydrolysis and polycondensation properties.

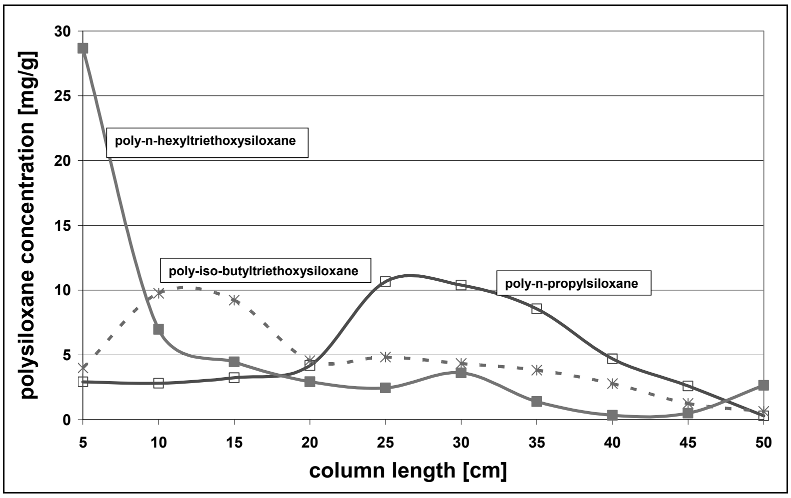

Figure 6: Distribution of polysiloxane in the column material as a function of the column length.

4 Discussion

Different experiments have been carried out in order to characterise the hydrolysis and polycondensation of different silanes in contact with cement based materials. The results confirm and extend the knowledge about the influence of the alkyl group on silane reactivity [7, 8, 9].

In the literature the kinetics of the silane hydrolysis is described as a first order reaction (equation 1) [7,10].

$$\frac{dc_{Silane}}{dt} = k \cdot c_{Water} \cdot c_{Silane} \tag{1}$$

with:

c_{Silane} = concentration of the silane [mol/l]

t = time of reaction [s]

k = reaction rate constant [s^{-1}]

For real systems, a water excess can be assumed so that the reduction of the water content during hydrolysis can be considered negligible. This leads to the formulation of the pseudo first order reaction in which the water content (c_{Water}) is incorporated in the reaction rate constant k* (equation 2).

$$\frac{dc_{Silane}}{dt} = k^{*} \cdot c_{Silane} \quad (2)$$

The hydrolysis constants k* for the different silanes resulting from the batch experiments are presented in Table 1.

Table 1: Hydrolysis constants of different silanes in an aqueous solution under the assumption that the hydrolysis is of a pseudo-first order type.

silane	K* $[10^{-3}\text{min}^{-1}]$
n-propyltriethoxysilane	54,8
Iso-butyltriethoxysilane	22,7
n-pentyltriethoxysilane	4,6
n-hexyltriethoxysilane	1,6
iso-octyltriethoxysilane	0,2

The results show that the longer the alkyl chain the slower the hydrolysis. This can be explained by two effects: first, that longer alkyl groups cause a steric effect; and, second, that they increase the inductive effects on the silicon atom. Electrons are shifted towards the silicon atom rendering it more negative and hence less reactive towards OH^{-} - ions [11].

This study is the first one in reporting the time-dependence of the **surface tension** of an aqueous solution of silanes. These experiments give additional information about the silane reaction and especially about the formation and the condensation reaction of silanols as intermediate products. Silanols consist of at least one hydrophilic head-group and hydrophobic tail-group (alkyl group) (Figure 7). Therefore it is likely that silanols form micelles, having a structure comparable to the one built up by surfactants [12]. In micelles the nonpolar part is oriented into the micelle while the polar part is oriented to the aqueous solution. The curves of the time-dependence of surface tension show a decrease after addition of silane due the formation of silanol. As long as the concentration of silanol is above a certain threshold value, the surface tension remains constant. This effect is a strong indication that micelle structures are formed and that the critical micelle concentration (cmc) of silanols in the liquid phase has been reached. The structure of micelles depends on that of the silanols. Polycondensation leads to a reduction of the silanol concentration to values lower than the cmc resulting in an increase of the surface tension.

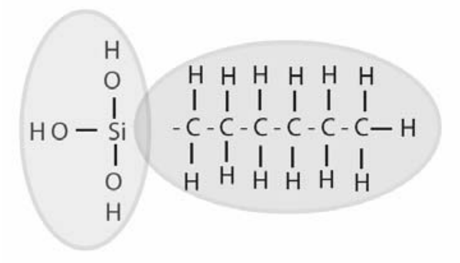

Figure 7: Schematic presentation of the surfactant structure of a silane triol

The longer the alkyl group the lower the slope of the curve of the time dependence surface tension corresponding to polycondensation. Hence, it can be assumed that the lifetime of silanols increases for increasing chain length of the alkyl group [13].

The variation of the surface tension of silanols having different alkyl groups corresponding to the “plateau-phase” matches well with that of the pure silanes (Table 2). In both cases, an increased surface tension is obtained for an increased chain length of the alkyl group.

Table 2: Surface tension of different silanes and corresponding silanols (according to [4])

	silane [mN/m]	silanol corresponding to the plateau-phase [mN/m]
n-propyltriethoxysilane	22.7	43
iso-butyltriethoxysilane	23.0	46
iso-octyltriethoxysilane	25.5	61

To characterise the properties of the polymer formed on the solid phase **sorption experiments** were carried out. These have shown that the adsorbed amount of polysiloxane is limited (q_{max}). This effect can be explained by the following hypothesis. The inner surfaces of the pores become more and more hydrophobic during the experiments, preventing the uptake of water containing reactive silicon compounds.

The polysiloxane having a short alkyl group cannot be removed from the solid phase by an organic solvent indicating a strong bonding. On the other hand, silanes with long alkyl groups form first a polysiloxane layer strongly bonded to the surface on to which further polymeric material is adsorbed. The latter can be removed by an organic solvent. However, after three months conditioning in dry conditions, no polysiloxane can be removed indicating that polymerisation has continued.

Results of **reactor experiments** carried out with different silanes confirm an influence of the type of silanes on the kinetics of the hydrolysis and the total amount of ethanol released (Figure 5). The ethanol release curve from n-propyltriethoxysilane is very similar to the breakthrough curve of pure ethanol indicating a very fast hydrolysis. The ethanol is released nearly at the same moment the silane enters the alkaline environment of the concrete matrix. The longer the alkyl groups of the silane molecules the slower the ethanol release. As mentioned above, this can be explained by steric and inductive effects.

Also the amount of ethanol released depends on the alkyl group of triethoxysilanes: silanes with short alkyl groups seem to release nearly the maximum amount of ethanol indicative of a complete hydrolysis. This is not the case for silanes having longer alkyl groups. The explanation can be found in the differences in hydrolysis and condensation rates for the different silanes. Hydrolysis is slowed down with increasing length of the alkyl groups, therefore condensation starts before the hydrolysis is completed. And silicone compounds having reactive groups are generated which then chemically bond to the solid particles of the concrete. Hydrolysis yields inversion of the silicon atom [13]. Because of the attachment of the silanol molecule to the mineral surface the inversion of the molecule is no longer possible and hence at least one ethoxy group remains on the molecule as hydrolysis cannot take place and the release of ethanol is diminished.

The distribution of the silicon polymers within the cement based solid phase of the column varies for different silanes due to differences in the condensation rate. Poly-n-propyltriethoxysilane is adsorbed further down in the column than the silane polymers with longer alkyl groups (Figure 6). The reason lies in the different tendencies of silanes to react with each other or with the surface of the solid phase. Silanes with short alkyl groups have generated many silanol groups after a short time, due to fast hydrolysis. This could cause a high affinity to a polycondensation with each other. So polysiloxanes are generated, which are initially not connected with the solid phase and transported through the column. This explains the penetration depth of poly-n-propyltriethoxysilane which gets immobilised at a deeper penetration depth. On the other hand, silanes with long alkyl groups form molecules with one or two silanol groups. The remaining ethoxy groups render the silicone molecule more basic than Si-O-H groups of the solid material which explains their preferential reaction with the substrate rather than with a silane triol. Therefore, their adsorption occurs at a short distance into the column.

5 Conclusions and outlook

From the results presented here the following conclusions can be drawn:

- The batch experiments are a powerful tool to analyse the kinetics of the silane hydrolysis. The differences in the hydrolysis kinetics as a function of the silane structure can be explained by steric and inductive effects.
- Intermediate products have an effect on the surface tension of the liquid phase which influences the transport efficiency during capillary absorption.
- The time-dependent development of the bonding strength of polysiloxanes on the surface is a function of the length of the alkyl group and the time elapsed from the initial reaction.
- The reactor experiments are useful to investigate reactive transport processes because the chemical reaction and the transport process can be separated. The transport of silane and its reaction products is determined by the kinetics of hydrolysis and condensation.

Results from experiments with varied silane concentration or pH values of the liquid phase and the addition of different solid phases (e.g. quartz, hardened cement paste, non-carbonated and carbonated concrete) will be reported in future papers.

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